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**Description**

This invention relates to a process for separating dissolved fluorine and/or fluorine compounds using an adsorbent which can remove selectively fluorine and or fluorine compounds dissolved at low concentrations in water at high efficiency. Further, the present invention relates to a separation process using an adsorbent capable of removing by adsorption fluorine and/or fluorine compounds dissolved in raw water for drinking water or industrial wastewater, said adsorbent being highly operable and economical, since it can be desorbed by a simple operation to be regenerated and used repeatedly.

In addition, the present invention also relates to a process for treating dissolved fluorine and/or fluorine compounds, more particularly to a closed treatment process which comprises recovering the regenerating solution to be recycled in carrying out adsorption and regeneration by use of said adsorbent.

Description of the prior art

Originally, in the natural world, fluorine occurs in very minute amounts, for example, at about 1.2 - 1.4 ppm in sea water, ordinarily about 0.1 to 0.3 ppm in river water, and such amounts will cause no trouble in the ecological environment. However, it has been known that fluorine concentration in underground water may sometimes exceed 100 ppm because of discharging of fluorine compounds by volcanic activity.

On the other hand, the amounts of fluorine and fluorine compounds used are increasing in these days and they are widely used in electronic industries for production of semiconductors or washing internally of cathode ray tubes, metal industries such as production of aluminum, chemical industries or ceramic industries. In the wastewater discharged from such industries, fluorine remains as fluorine or compounds such as fluorine compounds, and the fluorine concentration in the wastewater may sometimes reach several hundred ppm.

The water containing such a high concentration of fluorine, which can have various deleterious influences on human bodies and animals or vegetables as environmental water, must be maintained and managed so as to have as low level of fluorine as possible, and therefore it has been desired to establish an efficient and high technique for treatment of such water.

As a process for removing fluorine and fluorine compounds in industrial wastewater, it has generally been practiced to precipitate by separation as calcium fluoride having little solubility in water by use of a calcium salt such as slaked lime, calcium chloride, etc. However, calcium fluoride also has a solubility in water, and the fluorine concentration cannot be made 10 ppm or less even by an ideal treatment. Also, fluorine tends greatly to form complex ions with silicon, iron, aluminum in wastewater, and the calcium salts thereof have greater solubilities and hence it is very difficult to remove fluorine to low concentration by precipitation separation.

On the other hand, as a process for removing a minute amount of fluorine dissolved in water at less than 10 ppm, it has been practiced in the prior art to treat water by adsorption with an activated alumina or with the use of a combination of an ion-exchange resin and an activated alumina. However, in the activated aluminum adsorption process, the amount of fluorine adsorbed on the activated alumina is small, and also adsorption is affected by the co-existing ions such as carbonate ions, etc., whereby no expected removing effect can disadvantageously be obtained. In this connection, there is an attempt to remove fluorine by treating the solution, from which other co-existing ions have been removed by adsorption with an ion-exchange resin, with an activated alumina. However, in this case, harmless ions are also removed excessively to make the quality of water undesirable for drinking water, and also there is involved the problem of high cost in such treatment. Also, as an advanced treatment process of wastewater containing both fluorine and fluorine compounds, it has been proposed to subject the wastewater to the adsorption treatment by use of an anion exchange resin, after enhancement of selective adsorbability by converting the fluorine to fluorine compounds by the reaction with silicon (Japanese Laid-open Patent Publication No. 8582/1983) or iron, aluminum or zirconium (Japanese Laid-open Patent Publication No. 64181/1983). However, this process involves the problems such that the treatment steps become more complicated or that the conditions for high degree of treatment to a fluoride ion concentration of 1 ppm or less can be set with difficulty, because fluorine remains in wastewater due to the dissociation constant possessed by fluorine compounds.

Chemical Abstracts, Volume 86, No. 12, page 168 referring to SU-A-539 845 disclose a process for separating dissolved fluorine ions which comprises bringing a solution containing said ions into contact with a rare earth carbonate. However no other rare earth salts or rare earth oxides are mentioned as adsorbent. Moreover it is silent about selectivity and capacity of the adsorbent as well as about the adsorption of complex fluorine compounds.

GB-A-2 135 983 discloses the use of hydrated rare earth oxides for the selective adsorption of borate ions from solutions containing e.g. other ions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  etc. Borate ions are desorbed and regenerated for reuse by contacting the said oxides or hydroxides with an aqueous solution adjusted to pH about 2 to about 4, preferably in co-presence of an inorganic anion or an organic anion. The concentration of the co-present anions may differ depending on the ion species being appropriately about 0,5 to about 1.000 mM/l. Fluorine ions and sulfate ions are preferred for their great desorption effects.

As described above, under the present situation, neither the adsorbent capable of removing fluorine and fluorine compounds contained in minute amounts in solutions nor its treatment technique have satisfactorily been established.

#### Summary of the invention

An object of the present invention is to provide a process for separating dissolved fluorine and/or fluorine compounds by bringing a solution containing them dissolved therein into contact with an adsorbent capable of removing fluorine and or fluorine compounds dissolved at low concentrations, particularly an adsorbent capable of removing selectively and efficiently minute fluorine and fluorine compounds co-existing with various cations and anions in solution.

Another object of the present invention is to provide an economical separation process using an adsorbent which can adsorb fluorine and or fluorine compounds dissolved in solutions and which also allows use by efficient desorbing regeneration.

Still another object of the present invention is to provide an economical process for treating dissolved fluorine comprising the step of separating by adsorption of fluorine and/or fluorine compounds dissolved in solutions, the step of regenerating the adsorbent, the step of recovering of fluorine by precipitation and the step of recovering the regenerated solution.

A further object of the present invention is to provide a process for producing the adsorbent suitable for adsorption of dissolved fluorine and/or fluorine compounds.

The present invention provides a process for separating dissolved fluorine and/or fluorine compounds which comprises: bringing a solution having a pH of 2 to 7 and containing fluorine and/or fluorine compounds dissolved therein into contact with a hydrated rare earth oxide, a hydrous rare earth fluoride and/or a hydrous rare earth phosphate as the adsorbent.

The adsorbent used in the process of the present invention can adsorb fluorine and fluorine compounds selectively and at high efficiency and the adsorbed fluorine on said adsorbent can readily be desorbed to regenerate for reuse by bringing it into contact with an aqueous alkali solution of pH 10 or higher.

Further, the invention provides a process for treating dissolved fluorine, which comprises bringing an aqueous solution of pH 2 to 7 containing fluorine and/or fluorine compounds dissolved therein into contact with an adsorbent comprising a hydrated earth oxide, a hydrous rare earth fluoride and/or a hydrous rare earth phosphate to separate fluorine and/or fluorine compounds by adsorption, and bringing said adsorbent having adsorbed fluorine and/or fluorine compounds thereon into contact with an alkali solution of pH 10 to 14 to desorb the adsorbed fluorine and/or fluorine compounds, thereby regenerating said adsorbent.

Preferably the process comprises further a step of separating fluorine and/or fluorine compounds by addition of a precipitating agent for fluorine and/or fluorine compounds to the alkali solution containing desorbed fluorine and/or fluorine compounds. Preferably the alkali solution is recovered as a regenerating solution for the adsorbent having adsorbed fluorine and/or fluorine compounds thereon.

#### Brief description of the drawings

Fig. 1 shows the relationships between the removal percentage of fluoride ions, hexafluorosilicic ions, chloride ions, nitrate ions and sulfate ions dissolved in the aqueous solution by the hydrous cerium oxide of the present invention and pH.

Fig. 2 shows the relationship between pH of the solution and the desorption percentage when desorbing the hydrous yttrium fluoride having fluorine adsorbed thereon.

Fig. 3a is a X-ray diffraction spectrum of the hydrous cerium oxide of the present invention.

Fig. 3b is an infrared absorption spectrum of the hydrous cerium oxide of the present invention.

Fig. 4a is a X-ray diffraction spectrum of the yttrium hydroxide of the present invention.

Fig. 4b is an infrared absorption spectrum of the yttrium hydroxide of the present invention.

Fig. 5a is a X-ray diffraction spectrum of the hydrous yttrium fluoride of the present invention.

Fig. 5b is an infrared absorption spectrum of the hydrous yttrium fluoride of the present invention.

Fig. 6 shows an example of the fluorine treatment process of the present invention.

Detailed description of the invention

The adsorbent of the process according to present invention comprises a hydrated rare earth oxide, a hydrous rare earth fluoride and/or a hydrous rare earth phosphate of at least one metal selected from the group of rare earth elements. The adsorbent of the present invention is brought into contact with a fluorine dissolved water with pH ranging from 2 to 7 to adsorb fluorine and/or fluorine compounds selectively and at high efficiency, and the adsorbed fluorine on said adsorbent can readily be desorbed by contact with an aqueous alkali solution of pH 10 to 14 to regenerate the adsorbent for reuse.

The rare earth metal elements of the present invention include Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Of these rare earth metals, Y, La, Ce, Nd and Sm are preferred, and particularly Ce(IV) is most preferred for great adsorption capacity as well as negligible extent of low solubility in water.

The hydrous rare earth fluoride and the hydrous rare earth phosphate have a solubility of 10 mg/liter or less in pure water and show an excellent adsorption capacity. The hydrated rare earth oxides, hydrous rare earth fluorides and hydrous rare earth phosphates may be used either singly or as a mixture of two or more compounds.

Most preferred as the adsorbent are hydrous cerium oxide, hydrous cerium fluoride, yttrium hydroxide, hydrous yttrium fluoride, lanthanum hydroxide and hydrous lanthanum fluoride.

In the following, examples for the process for production of the adsorbent of the present invention are given.

Said hydrated rare earth oxide of the present invention can be obtained easily as the precipitate by, for example, adding an alkali solution into an aqueous solution of a salt such as a metal chloride, sulfate, nitrate, etc. and controlling the pH of the above aqueous salt solution. In controlling the pH, by selecting the metal and its salt employed, the solution thereof, the alkali employed and its solution, and the precipitate forming conditions such as the method for mixing the aqueous metal salt solution with the alkali solution and the speed of mixing, etc., hydrous oxides or hydroxides can be formed.

Preferably the hydrous rare earth oxide is obtained from a starting material of a mixture of rare earth chlorides.

Hydrous rare earth fluoride can be obtained (1) by the reaction of hydrofluoric acid with the hydrated oxide prepared by the above method or (2) by the reaction of hydrofluoric acid or an aqueous readily soluble fluoride with the aqueous solution of a metal salt, as already mentioned for the preparation of said hydrated rare earth oxide, to prepare said hydrous rare earth fluoride, followed by the reaction of an aqueous alkali solution such as aqueous sodium hydroxide, etc. with said hydrous rare earth fluoride.

Hydrous rare earth phosphate can be obtained as the precipitate by the reaction of the rare earth solution with the aqueous solution of soluble phosphate. Preferably the hydrous rare earth fluoride and/or the hydrous rare earth phosphate are obtained from a starting material of a mixture of rare earth chlorides. Most preferably the obtained adsorbent for the process of the invention is hydrous cerium phosphate.

In preparation of said hydrated rare earth oxide, said hydrous rare earth fluoride and said hydrous rare earth phosphate according to the above method, various kinds of metal ions other than the metal ions used in the preparation may be permitted to co-exist to form composite hydrated rare earth oxides, composite hydrous rare earth fluorides and composite hydrous rare earth phosphates. Examples of such metal which can co-exist may include Al, Cr, Co, Ga, Fe, Mn, Ni, Ti, V, Sn, Zr, Hf, Ge, Nb, Ta, Th, etc. These co-existing metal elements may be present in an amount of 40 mol % or less, more preferably 20 mol % or less, based on the total amount of metal elements present.

Also, the cations and anions to be used in the preparation as described above may also exist as a part of structure of the hydrated rare earth oxide, the hydrous rare earth fluoride and/or the hydrous rare earth phosphate of the present invention. These cations and anions which can co-exist may include, for example,  $\text{NH}_4$ , Na, K, Ca, Mg, Al,  $\text{SO}_4$ ,  $\text{NO}_3$ , F, Cl,  $\text{PO}_4$ ,  $\text{P}_2\text{O}_7$ ,  $\text{CrO}_4$ ,  $\text{BO}_3$ ,  $\text{SiO}_3$ ,  $\text{CO}_3$ , etc.

The structural characteristic of said hydrated rare earth metal oxide, said hydrous rare earth fluoride and said hydrous rare earth phosphate prepared by the above method is described below.

The structure of a hydrated rare earth oxide, a hydrous rare earth fluoride and a hydrous rare earth phosphate is not clear, but its chemical formula may be estimated as follows.

That is, concerning hydrated rare earth oxides, the chemical formulae for trivalent and tetravalent rare earth elements may be  $\text{Ln}(\text{OH})_3 \cdot x\text{H}_2\text{O}$  and  $\text{Ln}(\text{OH})_4 \cdot x\text{H}_2\text{O}$  or  $[\text{Ln}_2\text{O}_a(\text{OH})_{6-2a} \cdot x\text{H}_2\text{O}]_n$  and  $[\text{LnO}_b(\text{OH})_{4-2b} \cdot x\text{H}_2\text{O}]_n$ , respectively. On the other hand, the hydrous rare earth fluorides and the hydrous rare earth phosphates may be considered to be the above hydrated rare earth oxides, in which a part of all of OH groups are substituted with anions such as F and  $\text{PO}_4$ . (here, a part of Ln may be substituted with cations other than rare earth elements as mentioned above, and a part of (OH) group may be substituted with anions as

mentioned above). In these formulae,  $L_n$  represents a rare earth element, and  $a$  is an integer of 0 to 3,  $b$  and integer of 0 to 2 and  $x$  and  $n$  are positive numbers.

Of hydrated rare earth oxides, hydrous oxides refer to those which exhibit the same diffraction patterns as the corresponding metal oxides in X-ray diffraction, but have broad diffraction line widths due to poor crystallinity, having no specific thermal transition point and generating gradually thermal weight reduction with temperature elevation until becoming finally oxides with good crystallinity, while having a thermal weight reduction of 5 to 30 wt. %. In IR absorption spectrum, a broad absorption band based on the stretching vibration of hydroxyl group at around  $3400\text{ cm}^{-1}$  and 2 to 3 absorption bands based on deformation vibrations of hydroxyl group at  $1700 - 1300\text{ cm}^{-1}$  are exhibited.

On the other hand, hydroxides refer to those which exhibit diffraction pattern of corresponding metal hydroxides in X-ray diffraction and can thermally be converted into oxides at specific temperatures. In IR-absorption spectrum, sharp absorption bands at  $3500 - 3700\text{ cm}^{-1}$  inherent in metal hydroxides based on stretching vibration of hydroxyl group, broad absorption band at around  $3400\text{ cm}^{-1}$  and 2 to 3 absorption bands at  $1700 - 1300\text{ cm}^{-1}$  based on deformation vibration of hydroxyl group are exhibited.

Hydrous rare earth fluorides exhibit the same patterns as the corresponding rare earth fluorides or rare earth oxyfluorides in the X-ray diffraction, but have broad diffraction line widths due to poor crystallinity. Thermally, they have no specific transition point, and are converted to rare earth fluorides or rare earth oxyfluorides at higher temperature, for example, up to  $500^\circ\text{C}$ , and the thermal weight reduction thereby is 2 to 20 wt. %. In IR absorption spectrum, a broad absorption band based on the stretching vibration of the hydroxyl group at around  $3400\text{ cm}^{-1}$  and 2 to 3 absorption bands based on deformation vibrations of the hydroxyl group at  $1700 - 1300\text{ cm}^{-1}$  are exhibited.

As described above, the hydrated rare earth oxide and the hydrous rare earth fluoride of the present invention have respective inherent characteristics in X-ray diffraction, IR absorption spectrum and thermal properties, and their common characteristic is to have absorption bands at around  $1500\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$ , and the structure having said absorption bands is very important in exhibiting the effect of the present invention.

On the other hand, as for said hydrous rare earth phosphate, no specific diffraction line is exhibited in X-ray diffraction but only moderate scattered line is exhibited, having no thermal specific transition point, with the thermal reduction weight being 5 to 40 wt. %. In IR absorption spectrum a broad absorption band based on the stretching vibration of the hydroxyl group at around  $3400\text{ cm}^{-1}$ , 2 to 3 absorption bands based on the deformation vibration of the hydroxyl group at  $1700 - 1300\text{ cm}^{-1}$  and an absorption band based on phosphoric acid group at  $1000$  to  $1100\text{ cm}^{-1}$  are exhibited.

The thermal weight reduction as herein mentioned refers to the percentage reduction based on the original weight when a sample is heated at a rate of  $10^\circ\text{C}/\text{min.}$  from room temperature up to  $800^\circ\text{C}$  in the case of a hydrated rare earth oxide, or up to  $500^\circ\text{C}$  in the case of a hydrous rare earth fluoride or a hydrous rare earth phosphate.

The adsorbent in the present invention is a cake obtained by filtration of said hydrated rare earth oxide, said hydrous rare earth fluoride and/or said hydrous rare earth phosphate according the preparation method as described above, etc., or its dried powder and a molded product by molding these into any desired shape such as granules, filaments, strands, bands, plates, etc. by an appropriate method preferably carrying on a porous carrier, etc. Said molded product is very useful in enhancing practical absorbing operation.

As the material to be used as the carrier, various inorganic and organic materials capable of exhibiting the effect of the present invention can be used, but various organic polymeric materials are preferred in aspects of carrying workability, strength of carrier and chemical resistance.

Organic polymeric materials may include phenol resin, urea resin, melamine resin, polyester resin, diallyl phthalate resin, xylene resin, alkylbenzene resin, epoxy resin, epoxy acrylate resin, silicon resin, urethane resin, fluorine resin, vinyl chloride resin, vinylidene chloride resin, polyethylene, chlorinated polyolefin, polypropylene, polystyrene, ABS resin, polyamide, methacrylic resin, polyacetal, polycarbonate, cellulose resin, polyvinyl alcohol, polyimide, polysulfone, polyacrylonitrile, etc., and copolymers as mentioned above. Particularly preferable materials are those having appropriate water resistance, chemical resistance and great hydrophilic property, which are capable of forming porous structures, such as polyamide, cellulose resin, polysulfone, polyacrylonitrile, ethylene-vinyl alcohol copolymer, etc. Most preferably the form of the porous material is spherical.

Various known methods may be applicable for carrying the adsorbent on the above organic polymeric material. For example, in a solution having an appropriate polymer dissolved therein, particles of said hydrated rare earth oxide said hydrous rare earth fluoride and/or said hydrous rare earth phosphate may be suspended and formed into granules, filaments, strands or bands. Alternatively, an appropriate monomer for a polymer is polymerized by emulsion or suspension polymerization in the presence of said hydrated rare

earth oxide, said hydrous rare earth fluoride and/or said hydrous rare earth phosphate to be formed into granules. Further, it is also possible to mix and mold an appropriate polymer with said hydrated rare earth oxide, said hydrous rare earth fluoride and/or said hydrous rare earth phosphate and various extractable reagents, and extracting said agents with an appropriate solvent. In any of these cases, it is necessary to form a structure in which said hydrated rare earth oxide, said hydrous rare earth fluoride and/or said hydrous rare earth phosphate is sufficiently carried on the molded product so that it can practically not be leached away, and any method may be used, provided that such an object can be accomplished.

Of these methods, a particularly preferred method is to dissolve a hydrophilic polymer such as polyamide, cellulose resin, polysulfone, polyacrylonitrile, ethylenevinyl alcohol copolymer, etc. in an appropriate solvent, suspend said hydrated rare earth oxide, said hydrous rare earth fluoride and/or said hydrous rare earth phosphate in the resultant solution and coagulate the suspension into beads in water bath.

The beads obtained by this method have a porous structure, sufficient adsorption rate and physical strength and are suitable for carrying out adsorption and desorption operations according to fixed-bed or fluidized-bed engineering process.

Particularly, the amount of the polymer employed may be 5 to 50 wt. %, preferably 10 to 30 wt. %, of said hydrated rare earth oxide, said hydrous rare earth fluoride and/or said hydrous rare earth phosphate. At a level lower than 5 wt. %, no sufficient carrying effect can be exhibited and the strength is also insufficient, while an amount over 50 wt. % will markedly lower the adsorption rate.

The size and the void volume of the said beads have influences on the adsorbing action, particularly adsorption rate, of the adsorbent of the present invention. The bead size may preferably be 0.1 to 5 mm on an average, and the void volume 0.5 to 0.85.

The average particle size refers to the weight average particle size shown by the 50 % accumulated value in the accumulated distribution curve determined by screening with several kinds of mesh.

The void volume as mentioned in the present invention refers to a value of the change in volume ( $V_1 - V_0$ ) from the apparent volume ( $V_1$ ) under dry state of said particles to compressed volume ( $V_0$ ) during compression relative to said apparent volume, namely represented by  $(V_1 - V_0)/V_1$ . Here, the apparent volume ( $V_1$ ) is the volume of a certain weight of beads measured by the mercury picnometer method, while the compressed volume ( $V_0$ ) is the volume of the same weight of sample by compression molding at 100 °C under a pressure of 50 kg/cm<sup>2</sup>. If the void volume is less than 0.5, the adsorption rate will be too slow, while a void volume over 0.85 will make the strength insufficient.

Also, the properties and the surface conditions of the particles of said hydrated rare earth oxide, said hydrous rare earth fluoride and said hydrous rare earth phosphate are very important in exhibiting the effect of the present invention, and it is preferable to control the amount of structural water and adhered water and particle sizes and agglomeration degree of the particles, so that the particle size may be as small as possible, namely a primary particle size of 0.01  $\mu$  to 1  $\mu$  as average particle size, particularly preferably 0.01 to 0.5  $\mu$ m, the agglomerates being also fine particles with a low degree of agglomeration with sizes of about 0.05 to 10  $\mu$ .

The method for adsorbing fluorine and/or fluorine compounds onto said adsorbent may be any method which can bring said hydrated rare earth oxide, said hydrous rare earth fluoride and/or said hydrous rare earth phosphate into contact with water containing fluorine and fluorine compounds dissolved therein. For example, there may effectively employed the method in which a cake, powder or molded product thereof as described above of said hydrated rare earth oxide said hydrous rare earth fluoride and/or said hydrous rare earth phosphate is added and dispersed in said water, or the method in which said water is passed through a column filled with said molded product or powder.

The hydrated rare earth oxide hydrous rare earth fluoride and hydrous rare earth phosphate, which is the fluorine adsorbent of the present invention, has also excellent adsorption capacity even when fluorine may exist in the form of fluorine compounds, and can remove fluorine comprehensively from the fluorine containing water in which both of fluoride ions and fluorine compounds co-exist. The fluorine compounds existing in water may include hexafluorosilicic ion, fluoroboric ion, hexafluoroaluminum ion, hexafluoroferric ion, hexafluorotitanium ion, hexafluorozirconium ion, etc. and these may be dissolved either singly or as a mixture of two or more kinds in water. Particularly, fluorine exists frequently as hexafluorosilicic ion, and it can excellently be adsorbed by use of the hydrous cerium oxide of the present invention at pH 7 or lower.

The mechanism in which the hydrated rare earth oxide, hydrous rare earth fluoride and/or hydrous rare earth phosphate of the adsorbent in the present invention adsorbs fluorine is due to anion exchange between the hydroxyl groups existing on the fluorine adsorbent and the dissolved fluoride or fluorine compounds. The hydroxyl groups existing on said fluorine adsorbent are rich in activity and undergo exchange with various dissolved anions such as fluoride ions, fluorine compounds, chloride ions, nitrate ions, sulfate ions, etc. when the pH of the aqueous solution is low, while they are retained as hydroxyl

groups when the pH is high. That is, when the pH of the aqueous solution in which various anions are dissolved is low, various anions are fixed on said adsorbent, while said anions fixed on said adsorbent are dissolved-out into the aqueous solution when the pH is high.

For example, when using the hydrous cerium oxide in the process of the present invention, the relationship between the adsorption capacity of said adsorbent for fluoride ions, hexafluorosilicic acid, chloride ions, nitrate ions and sulfate ions and the pH of the solution during adsorption shows that the adsorption capacity is greater on the acidic side for each ion, as shown in Fig. 1. Particularly, in the case of fluoride ions, the adsorption amount is abruptly increased at pH 7 or lower of the solution, but in the case of other ions such as chloride ions, no abrupt increase in adsorption amount is observed unless at pH 4 or lower.

Accordingly, when fluoride ions co-exist with other ions such as chloride ions, fluoride ions can selectively be adsorbed at pH 2 - 7 of the solution. Besides, the adsorption capacity for said ions is markedly greater as compared with other ions. In adsorption of fluoride ions by said adsorbent, preferably pH of the solution is 2 to 7. At a pH lower than 2, the solubility of said adsorbent is too high, while adsorption capacity is too small at a pH higher than 7.

The fluorine adsorbent used in the process of the present invention is very excellent in fluoride ion selectivity. More specifically, in a solution containing chloride ions, nitrate ions and sulfate ions at the same concentration as the fluoride ions, the selectivity relative to other anions than fluoride ions, when said aqueous solution has pH 5 during adsorption equilibrium, is as high as  $1 \times 10^2$  to  $1 \times 10^3$  for selectivity coefficient of fluoride ions relative to chloride ions ( $F/Cl$ ),  $2 \times 10^2$  to  $5 \times 10^3$  for selectivity coefficient of fluoride ions relative to nitrate ions ( $F/NO_3$ ), and  $3 \times 10$  to  $2 \times 10^2$  for selectivity coefficient of fluoride ions relative to sulfate ions ( $F/SO_4$ ).

The selectivity coefficient as mentioned in the present invention as represented relative to, for example, chloride ions is represented by the following formula:

$$K(F/Cl) =$$

$$\frac{[\text{Total fluoride conc. in adsorbent (meq/g-adsorbent)}] \times [\text{Total chloride ion conc. in aqueous solution (mmol/liter)}]}{[\text{Total fluoride conc. in aqueous solution (mmol/liter)}] \times [\text{Total chloride ion conc. in adsorbent (meq/g-adsorbent)}]}$$

..... Formula (I)

The saturated adsorption amount per unit weight of the fluorine adsorbent used in the process of the present invention is correlated with the fluoride ion concentration in the solution. For example, in the case of hydrous cerium oxide, if the pH of the aqueous solution during adsorption equilibrium is 5, the saturated adsorption amounts of fluoride on said fluoride ion adsorbent are 1.0 mmol/g-adsorbent, 2.0 mmol/g-adsorbent and 3.8 mmol/g-adsorbent at the fluoride ion concentrations in the aqueous solution of 0.01 mmol/liter, 0.1 mmol/liter and 1.0 mmol/liter, respectively. Accordingly, when removing by adsorption fluoride ions by use of said fluorine adsorbent, a suitable mixing ratio of said fluorine adsorbent and the fluoride ion containing water can be set depending on the initial concentration of fluoride ions and the target concentration thereof. For example, in the case when the hydrous cerium oxide having the above adsorption capacity is employed and the initial concentration of fluoride ions is 2 mmol/liter (38 ppm) and the fluoride ion concentration of the fluoride ion containing water is aimed at 0.8 mmol/liter (15 ppm), one gram of said adsorbent may be mixed with 2.8 liter of said aqueous solution and said mixture may be adjusted to pH 5.

The adsorbent having adsorbed fluoride ions thereon in the process of the present invention can also eliminate fluoride ions through contact with an alkali solution to be provided repeatedly for adsorption operations. In the above desorption operation, the amount of fluoride ions adsorbed on said adsorbent, the desorption percentage and fluoride ion concentration in the desorbing solution depend on the pH of the desorbing solution to be contacted, the mixing ratio of the adsorbent and the kind of desorbing solution and the solution temperature. For example, when employing the hydrous yttrium fluoride in the process of the present invention, the desorption percentage will be increased abruptly with the contact pH of the desorbing solution as shown in the relationship between the contact pH of the desorbing solution and the desorption percentage shown in Fig. 2. Therefore, the contact pH of the desorbing solution in the desorption operation may preferably be 10 or higher, more preferably 12 or higher. At a pH lower than 10, the desorption percentage is very low.

In the above desorption operation, for the aqueous alkali solution, inorganic alkalis such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, and organic amines may preferably be used. Sodium hydroxide and potassium hydroxide are particularly preferred for great desorption percentage. The alkali solution may have a concentration of 0.01 mol/liter or higher, preferably 0.05 mol/liter or higher.

As the method for desorbing fluorine and/or fluorine compounds fixed on the adsorbent in the process of the present invention, there may be employed any method which can bring said adsorbent into contact with an aqueous alkali solution, namely a similar method as in the adsorption method described above.

In the following, the process for treatment of water containing dissolved fluorine and/or fluorine compounds by use of said adsorbent is described for respective steps. The treatment process included in the present invention comprises the four kinds of the steps shown below. In these steps, only the step (1) is essential and the step (2), the steps (2) + (3), or the steps (2) + (3) + (4) may be combined with the step (1), if desired:

(1) the adsorption step of bringing water containing fluorine and/or fluorine compounds into contact with said adsorbent to separate fluorine by adsorption;

(2) the desorption and regeneration step by bringing the resultant adsorbent into contact with a regenerating solution;

(3) the fluorine recovery step which recovers fluorine from the desorbed solution by precipitation and separates the filtrate therefrom; and

(4) the regenerating solution recovery step in which the filtrate is adjusted for the regenerating solution in the step (2).

The adsorption step (1) in the present invention comprises adjusting the pH of the water containing fluorine and/or fluorine compounds dissolved therein to the suitable condition for adsorption of pH 2 to 7, and then bringing the water into contact with said adsorbent to adsorb fluorine and/or fluorine compounds adsorbed thereon.

The temperature in the above adsorption operation has an influence on the adsorption rate, and heating may effectively be conducted. However, even at normal temperature, the adsorbent has practically sufficient adsorption rate, and adsorption may be possible at 5 to 90 °C, practically preferably at 20 to 60 °C. The contact time, which may depend on the method of contact and the adsorbent employed, may be generally about one minute to 3 days before saturation of the adsorbed amount, but practically one to 60 minutes. These conditions of temperature and time may also be applicable for the desorption and regeneration operation as hereinafter described.

The next desorption and regeneration step is carried out by bringing the adsorbent having fluorine and/or fluorine compounds adsorbed thereon into contact with an alkali solution. The desorption percentage depends on the concentration of fluorine and/or fluorine compounds adsorbed on the adsorbent, the pH and the temperature of the alkali solution. Particularly, the influence of the pH of the alkali solution is great, and desorption may be possible at pH 10 or higher, preferably 12 or higher, more preferably 13 or higher.

In the above desorption operation, for the aqueous alkali solution, inorganic alkalis such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, etc. organic amines may preferably be used. Particularly, sodium hydroxide and potassium hydroxide are preferred for great desorption efficiency.

The amount of the alkali required for desorption of fluorine and/or fluorine compounds may be about one equivalent or more, preferably 1.3 equivalent or more, of the fluorine atoms to accomplish 100 % adsorption percentage. Accordingly, the fluorine concentration in the eluate can be made greater as the pH of the alkali solution is greater, whereby fluorine compounds and/or the alkali solution can more easily be recovered from the eluate.

When these alkali solutions are brought into contact with the adsorbent having fluorine and/or fluorine compounds adsorbed thereon, the fluorine and/or fluorine compounds will be desorbed through the ion exchange reaction, whereby the eluate after desorption will be neutralized to lower pH.

In the present invention, according to, further the fluorine recovery step (3) and the regenerating solution recovery step (4), by removing fluorine as the precipitates of insoluble fluoride salts, fluorine can be separated by precipitation as the solid and the filtrate can be provided for reuse as the regenerating solution. For removing fluorine by separation as the precipitates of fluoride salts, there are preferably employed known precipitating agents such as salts, e.g. chlorides, oxides, hydroxides, of calcium, magnesium, aluminum, etc. in an equivalent amount, preferably 1 to 4-fold equivalent, of fluorine. If the amount added is less than equivalent, the removal efficiency to be precipitated as fluoride will be lowered, while an amount over 4-fold equivalent will be uneconomical, since the removal efficiency cannot substantially be changed. The pH of the eluate in removing by separation may preferably 6 or higher, and further pH 12 or higher, preferably 13 or higher in the case of recovering the alkali solution from the eluate as the regenerating solution as hereinafter described. If the pH during precipitation treatment is smaller than 6, the



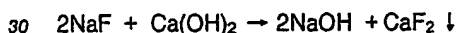
solubility of said metal compound becomes greater to lower the precipitation separation efficiency and, if the pH during recovery of the alkali solution is lower than 12, the efficiency of the alkali recovery will undesirably be lowered. The most suitable precipitating agent is a calcium compound and, when fluorine compounds are removed by precipitation as calcium compounds, other than calcium ions, aluminum sulfate or phosphates may also be permitted to co-exist, whereby the precipitation separation efficiency of the fluorine compounds in the eluate can be enhanced.

Here, as the conditions for the precipitation separation, the reaction time may be 10 minutes or longer, and the reaction temperature may be at around normal temperature to effect sufficiently rapid reaction, and no heating is particularly required. Also, for enhancing the precipitation separation, a known polymeric agglomerating agent may also preferably be added.

In the supernatant or the filtrate separated by precipitation, fluorine and/or fluorine compounds may be sometimes contained at a fluorine concentration of about 8 ppm or even to some ten ppm. Therefore, when its amount is small, it can be recycled to the adsorption step or diluted to be discharged as wastewater, or alternatively used as the water for make-up of the alkali solution for desorption. However, the most preferable method is to recover it as the alkali solution for desorption and regeneration of the adsorbent for reutilization.

The regenerating solution recovery step (4) may be conducted by adding calcium hydroxide in an amount of 1 to 4-fold equivalent of the fluorine in the eluate, while maintaining the pH in the eluate as described at 12 or higher, preferably 13 or higher, thereby separating the supernatant or the filtrate from the fluorine compounds by precipitation for use as the regenerating solution of the subsequent adsorption. Excessive calcium hydroxide may be used in an amount corresponding to its solubility as the regenerating solution. Further, when an alkali solution with concentration of pH 13 or higher is required, an alkali such as sodium hydroxide or potassium hydroxide is added to said filtrate to adjust pH to a desired value. These inorganic alkalis for maintaining the eluate at 13 or higher can be recovered in almost all the amounts, and therefore in the case of reutilization after the second time, a small amount thereof may be supplemented to adjust the pH of the regenerating solution to a desired value to an economical advantage.

For example, when calcium hydroxide is used in the regenerating solution and fluorine exists as sodium fluoride, a highly concentrated alkali solution can be recovered following the following reaction:



This reaction can proceed efficiently at pH 12 or higher, preferably at pH 13 or higher.

The alkali solution recovered here contains fluorine corresponding to the solubility of the fluoride, generally about 20 ppm of fluorine concentration, but it has no deleterious influence on the efficiency of the desorption regeneration, since the fluorine concentration in the eluate can be made as high as some thousand ppm. Thus, the treatment process of the present invention is characterized by separating efficiently the fluorine and/or fluorine compounds dissolved at low concentrations and concentrating to higher concentration by elution of the adsorbed fluorine with an alkali solution to take calcium compounds out of the system, which calcium compounds may also be used as the starting material for production of fluorine.

Also, the alkali solution recovered here contains calcium ions corresponding to the solubility and therefore, when brought into contact as such with the adsorbent having fluorine adsorbed thereon, precipitation of metal fluorides may sometimes be formed. Accordingly, it is effective to remove calcium ions previously. For this purpose, conventional methods may be applicable, but a preferable method is to bring the alkaline solution into contact with a cation exchanger. Further, since the adsorbent of the present invention is an amphoteric ion exchanger capable of adsorbing also calcium ions in an alkaline region, the same adsorbent used in fluorine adsorption can also effectively be used for adsorption removal of calcium ions in the regenerating solution.

The adsorbent subjected to desorbent regeneration through contact with an alkali solution should desirably be adjusted to pH suitable for the adsorption operation prior to the adsorption operation. The alkali component adhered on the adsorbent can be removed by washing the adsorbent with water or dilute acid, and it is generally effective to contact the adsorbent with an acid such as hydrochloric acid, sulfuric acid or nitric acid of 0.001 N to 1 N.

Referring now to the drawing, an embodiment of the process of the present invention is to be described. Fig. 6 shows an embodiment for practicing the process of the present invention, by which the present process is not limited. In Fig. 6, the fluorine containing solution a is adjusted at pH 5 in the reservoir 1, then delivered to the adsorption column 2 filled with said adsorbents, wherein fluorine is adsorbed to give

treated water b. When the fluorine concentration reaches a certain set value (breakthrough point), the adsorption step is completed and followed by the desorption regeneration step, and an alkali solution c of pH 10 or higher is delivered to the adsorption column 2 to elute the fluorine adsorbed, thereby forming an eluate d. The pH of the eluate d is 6 to 7 and the fluorine concentration becomes 1,000 to 5,000 ppm or even higher depending on the concentration of the said alkali solution. The eluate d is delivered to the precipitation tank 3, where calcium hydroxide is added thereto to form precipitates of calcium fluoride. The precipitates formed are taken out as calcium fluoride. The supernatant e in the precipitation tank is delivered to the regenerating tank 4, where it is adjusted to pH 10 or higher for reuse as the regenerating solution c.

In the present invention, when it is desired to perform treatment of the fluorine containing waste liquor continuously, two or three or more of fluorine adsorbing columns may be used and running can be operated by switching the adsorption and the desorption regeneration steps. In some cases, the process of the present invention can be practiced even by the multi-stage fluidized bed process, the moving bed process or the batch adsorption process.

The present invention is described in more detail by referring to the following Examples.

The adsorption amount, the removal percentage and the desorption percentage in the specification were determined according to the formulae shown below:

Adsorption amount (mmol/g-adsorbent)=

$$\frac{(\text{Initial conc.} - \text{Conc. after adsorption}) (\text{mmol/liter})}{\text{Amount of adsorbent (g)/liquid amount (liter)}}$$

Removal percentage (%)=

$$\left(1 - \frac{\text{Conc. after adsorption (mmol/liter)}}{\text{Initial conc. (mmol/liter)}}\right) \times 100$$

Desorption percentage (%)=

$$\frac{\text{Liquid amount (liter)} \times \text{conc. (mmol/liter)}}{\text{Amount of adsorbent (g)} \times \text{adsorption amount (mmol/g)}} \times 100$$

#### Example 1

An example of the pH dependency of the capacity of absorbing fluoride ions of the hydrous cerium oxide used in the process of the present invention (thermal weight reduction: 15.2 %, average particle size of primary particles: 0.08  $\mu$ , average particle size of agglomerated particles: 0.4  $\mu$ , X-ray diffraction: Fig. 3a, IR spectrum: Fig. 3b) is shown.

Hydrofluoric acid and hydrosilicofluoric acid were diluted with distilled water, respectively, to prepare fluoride ion containing water with respective fluoride ion concentrations of 2 mmol/liter (38 ppm), and each of said aqueous solutions was mixed with said adsorbent at a proportion of 1g-adsorbent/one liter, followed by stirring. Said mixture was adjusted to a predetermined pH with addition of 0.1 N aqueous sodium hydroxide solution. After 2 hours, the concentration of fluoride ions dissolved in the mixture was measured by ion chromatography. The result is shown in Fig. 1 as the relationship between the pH of the solution and the percentage of fluoride ions removed.

As reference examples, the results of the same experiments conducted for chloride ions, nitrate ions and sulfate ions are shown in Fig. 1.

#### Preparation of hydrous cerium oxide

Cerium chloride was dissolved in distilled water and an aqueous hydrogen peroxide in amount equivalent to cerium was added to the solution, followed by stirring. Then, the mixture was adjusted to pH 9 with addition of ammonia water. Thereafter, excessive hydrogen peroxide was decomposed by heating the mixture at 85 °C, and then the mixture aged overnight. After filtration, the product was dried in an air bath at

50 °C for 2 days.

## Examples 2 - 6

5 Examples of adsorption capacities of the adsorbents used in the process of the present invention for fluoride ions are shown.

A fluoride ion containing water (2 mmol/liter, 38 ppm) was prepared similarly as in Example 1, and said aqueous solution was mixed with each of hydrous cerium oxide (the same substance as in Example 1), yttrium hydroxide (prepared as described below, thermal weight reduction: 25%, average particle size of  
10 primary particles: 0.1  $\mu\text{m}$ , average particle size of agglomerated particles: 1  $\mu\text{m}$ , X-ray diffraction: Fig. 4a, IR absorption spectrum: Fig. 4b), hydrous yttrium fluoride (prepared as described below, thermal weight reduction: 25%, average particle size of primary particles: 0.03  $\mu\text{m}$ , average particle size of agglomerated particles: 1  $\mu\text{m}$ , X-ray diffraction: Fig. 5a, IR absorption spectrum: Fig. 5b), hydrous rare earth oxides mixture (prepared as described below, thermal weight reduction: 18%, average particle size of primary  
15 particles: 0.05  $\mu\text{m}$ , average particle size of agglomerated particles: 1  $\mu\text{m}$ ), acidic hydrous cerium phosphate (prepared as described below, thermal weight reduction: 22%, average particle size of primary particles: 0.12  $\mu\text{m}$ , average particle size of agglomerated particles : 2  $\mu\text{m}$ ) and hydrous cerium pyrophosphate (comparative example 3, prepared as described below, thermal weight reduction: 17%, average particle size of primary particles: 0.15  $\mu\text{m}$ , average particle size of agglomerated particles: 2  $\mu\text{m}$ ) at proportions of one  
20 liter/1g-adsorbent and 3 liters/g-adsorbent, respectively, followed by stirring. To each of the mixtures, 0.1 N aqueous sodium hydroxide solution or 0.1 N hydrochloric acid was added to adjust the pH to 5. After 2 hours, the concentration of the fluoride ions dissolved in said solution was measured according to the same method as in Example 1, and the percentage of fluoride ions removed and the amount of adsorption were calculated therefrom. The results are shown in Table 1.

25 For comparative purpose, the same experiments as in Examples 2 - 7 were also conducted for activated alumina (commercial product, fillers for gas chromatography) and hydrous titanium hydroxide (commercial product). The results are also shown in Table 1.

30

35

40

45

50

55

Table 1

	Adsorbent	Mixing ratio			
		1 l/g-adsorbent	3 l/g-adsorbent	1 l/g-adsorbent	3 l/g-adsorbent
		Removal percent- age (%)	Adsorbed amount (mmol/g)	Removal percent- age (%)	Adsorbed amount (mmol/g)
5					
10	Example 2 Hydrous cerium oxide	98	1.96	58	3.47
	Example 3 yttrium hydro- xide	93	1.86	73	4.35
15	Example 4 Hydrous yttr- ium fluoride	98	1.96	63	3.77
	Hydrous rare earth oxides	96	1.92	60	3.60
20	Example 5				
	Example 6 Acidic hydrous cerium phosphate	74	1.48	35	2.10
25	Compara- tive example 3 Hydrous cerium pyrophosphate	49	0.98	20	1.21
	Compara- tive example 1 Activated alumina	43	0.85	16	0.94
30	Compara- tive example 2 Hydrous titanium oxide	35	0.70	14	0.82
35					

Method for preparation of adsorbent 1 (Example 3):

Yttrium hydroxide: Yttrium chloride was dissolved in distilled water and an aqueous sodium hydroxide was added to adjust the resultant solution to pH 9. After aging overnight, the product was thoroughly washed with distilled water and dried at 110 °C.

Method for preparation of adsorbent 2 (Example 4):

Hydrous yttrium fluoride: Yttrium chloride was dissolved in distilled water and the resultant solution was adjusted with ammonia water to pH 9. To the precipitates formed were added hydrofluoric acid in an amount of 3-fold equivalents or more of yttrium. After aging overnight, the precipitates were thoroughly washed with distilled water, filtered and dried at 60 °C. One gram of said precipitates was suspended in 100 ml of 0.1 N aqueous sodium hydroxide, washed with water, filtered and dried at 60 °C.

Method for preparation of adsorbent 3 (Example 5)

Hydrous rare earth oxides mixture: Rare earth chlorides mixture were dissolved in distilled with water and stirred with addition of aqueous hydrogen peroxide in an amount equivalent to rare earth, followed by adjustment to pH 9 with addition of ammonia water. Then, excessive hydrogen peroxide was decomposed by heating the mixture at 85 °C and, after cooling, the mixture was adjusted to pH 4 with addition of

hydrochloric acid. After aging overnight, the product was washed thoroughly with distilled water and dried at 60 °C.

The composition of Y, La and lanthanides in said rare earth chlorides mixture is shown in Table 2.

Table 2

(Composition of rare earth chlorides: calc'd on oxides)

10	La <sub>2</sub> O <sub>3</sub>	25.15 wt. %
	Ce <sub>2</sub> O <sub>3</sub>	51.91 wt. %
	Pr <sub>6</sub> O <sub>11</sub>	5.12 wt. %
15	Nd <sub>2</sub> O <sub>3</sub>	16.07 wt. %
	Sm <sub>2</sub> O <sub>3</sub>	1.02 wt. %
	Eu <sub>2</sub> O <sub>3</sub>	0.19 wt. %
20	Gd <sub>2</sub> O <sub>3</sub>	0.17 wt. %
	Y <sub>2</sub> O <sub>3</sub>	0.04 wt. %

Method for preparation of adsorbent 4 (Example 6):

30 Acidic hydrous cerium phosphates: An aqueous ceric nitrate solution was added to an aqueous nitric acidic solution of disodium hydrogen phosphate. The gel precipitates were washed by decantation several times, and immersed in 1 N aqueous sodium hydroxide solution for 2 hours, washed with water and dried at 100 °C.

Method for preparation of adsorbent 5 (Comparative example 3):

35 Hydrous cerium pyrophosphate: To an aqueous cerous chloride was added an aqueous sodium pyrophosphate, and the mixture was aged overnight. The precipitates were thoroughly washed with distilled water, then immersed in 1N aqueous sodium hydroxide and washed with water, followed by drying at 100 °C.

40 Examples 8 - 10

Examples of ion selectivity of the adsorbents used in the process of the present invention are shown.

45 An aqueous mixed acid was prepared by diluting hydrofluoric acid, hydrochloric acid, nitric acid and sulfuric acid to each 2 mmol/liter concentration of fluoride ions, chloride ions, nitrate ions and sulfate ions. Said aqueous mixed acid was mixed with each 1g-adsorbent/one liter of hydrous cerium oxide (the same substance as in Example 1), yttrium hydroxide (the same substance as in Example 3) and hydrous yttrium fluoride (the same substance as in Example 4), respectively, followed by stirring. To said mixture was added an aqueous 0.1 N sodium hydroxide to adjust the mixture to pH 5. After two hours, the concentrations of fluoride ions, chloride ions, nitrate ions and sulfate ions in said solution were measured according to the same method as in Example 1 to determine the amounts of respective ions adsorbed on respective adsorbents.

55 From the results of measurements, the coefficients of selectivity of respective adsorbents for fluoride ions relative to chloride ions, nitrate ions and sulfate ions were calculated from the formula (I). The results of measurements and the amounts adsorbed are shown in Table 3a, and the coefficients of selectivity in Table 3b.

Table 3a

	Adsorbent	F		Cl		NO <sub>3</sub>		SO <sub>4</sub>	
		L*1	S*2	L	S	L	S	L	S
5									
10	Example 8 Hydrous cerium oxide	0.27	1.73	1.94	0.06	1.97	0.03	1.66	0.34
	Example 9 Yttrium hydroxide	0.44	1.56	1.94	0.06	1.97	0.03	1.92	0.08
15	Example 10 Hydrous yttrium fluoride	0.11	1.89	1.92	0.08	1.99	0.01	1.72	0.28

\*1) L=liquid; fluoride ion conc. in sample water (mmol/liter)

\*2) S=solid; adsorbed amount (mmol/g-adsorbent)

Table 3b (Selectivity coefficient)

25		<u>F/Cl</u>	<u>F/NO<sub>3</sub></u>	<u>F/SO<sub>4</sub></u>
	Example 8	207	421	31
	Example 9	115	233	85
30	Example 10	421	3420	106

## Example 11

Examples of the pH dependency of desorption percentage in the desorbing regeneration operation of the adsorbent of the present invention with an aqueous alkaline solution is shown.

The hydrous yttrium fluoride adsorbed previously with 5.4 mmol/g-adsorbent of fluoride ions was mixed with 0.01 to 1.0 N aqueous sodium hydroxide solutions, respectively, at a proportion of 10 g-adsorbent/liter, stirred, and, after 2 hours, the pH and the ion concentration of the mixture were measured (according to the same method as in Example 1). The results are shown in Table 4 and Fig. 2.

Table 4

45		<u>NaOH conc. (N)</u>	<u>pH of mixture</u>	<u>Desorption</u> <u>percentage(%)</u>
	Example 11-a	0.01	10.10	16.7
50	Example 11-b	0.05	12.37	55.0
	Example 11-c	0.10	12.85	66.6
	Example 11-d	0.50	13.55	90.2
55	Example 11-e	1.0	13.83	100

## Examples 12 - 14

Examples of the desorbing regeneration operations by use of various alkali species in the desorbing regeneration operations of the adsorbents of the invention are shown.

- 5 The hydrous yttrium fluoride adsorbed previously with 5.4 mmol/g-adsorbent of fluoride ions was mixed with 0.5 N aqueous sodium hydroxide, aqueous potassium hydroxide and ammonia water, respectively, at a proportion of 10 g-adsorbent/liter, stirred, and, after 2 hours, the pH and the ion concentration of the mixture were measured (according to the same method as in Example 1). The results are shown in Table 5.

Table 5

	<u>Alkali species</u>	<u>pH</u>	<u>Desorption percentage(%)</u>
15	Example 12	NaOH	13.55
			90.2
	Example 13	KOH	13.50
			85.0
20	Example 14	NH <sub>4</sub> OH	12.20
			50.0

## 25 Examples 15 - 17

Examples of capacities for adsorption of fluoride complex ions of the adsorbents of the present invention are shown.

- 30 An aqueous solution with the total fluorine concentration of 100 ppm comprising fluoride complex ions in aqueous solution was prepared. As the fluoride complex ions, sodium silicofluoride (reagent, special grade), titanium potassium fluoride (reagent) or cryolite (reagent) was employed. Said mixed aqueous solution was mixed with hydrous cerium oxide (the same substance as in Example 1) at a proportion of 1g-adsorbent/liter and adjusted to pH 5, followed by stirring for 24 hours.

- 35 The respective ions in the aqueous solution were measured to measure the residual fluorine concentrations in water and determine the removal percentages of fluorine. The results are shown in Table 6.

Table 6

	<u>Complex fluoro anion</u>	<u>Amount of fluo- rine adsorbed (mg-F/g-adsor- bent)</u>	<u>Total fluo- rine removal percentage (%)</u>
40			
45	Example 15	Hexafluorosilicic.	83
			83
	Example 16	Hexafluoroaluminum	91
			91
50	Example 17	Hexafluorotitanium	85
			85

## 55 Example 18

An example of the pH dependency of desorption percentage in the desorbing regeneration operation of

the adsorbent of the present invention with an aqueous alkaline solution is shown.

The hydrous yttrium fluoride adsorbed previously with 0.82 mmol/g-adsorbent of hexafluorosilicic ions was mixed with 0.01 to 1.0 N aqueous sodium hydroxide solutions, respectively, at a proportion of 10 g-adsorbent/liter, stirred, and, after 2 hours, the pH and the ion concentration of the mixture were measured (according to the same method as in Example 1). The results are shown in Table 7.

Table 7

		<u>NaOH conc. (N)</u>	<u>pH of mixture</u>	<u>Desorption percentage(%)</u>
15	Example 18-a	0.01	10.34	23
	Example 18-b	0.05	12.46	59
	Example 18-c	0.10	12.88	74
20	Example 18-d	0.50	13.53	93
	Example 18-e	1.0	13.86	100

#### Example 19

An example of adsorption and desorption operations performed by use of the bead-like adsorbent comprising particulate hydrous cerium oxide carried on a polyacrylonitrile resin is shown.

A fluoride ion containing water with a fluoride ion concentration of 10 mmol/liter was prepared by diluting hydrofluoric acid with distilled water. One liter of said solution was mixed and stirred with 7.0 ml as bulk volume of said adsorbent (bead size 1.0 - 0.5 mm $\phi$ , void volume ratio: 0.65). To the mixed solution, an aqueous sodium hydroxide was added to adjust pH to 5. After 5 hours, the fluoride ion concentration in said mixed solution was measured according to the same method as in Example 1, and the amount adsorbed was calculated therefrom. The results are shown in Table 8.

Subsequently, 20 cc (as bulk volume) of the above adsorbent after adsorption were filled in a glass column of 10 mm  $\phi$ , and an aqueous 0.1 N sodium hydroxide was passed therethrough at the rate of 40 ml/hour for 8 hours. The effluent from the column was recovered in fractions every 30 minutes, and the fluoride ion concentration in said effluent was measured according to the same method as in Example 1. From the results of measurement, the total amount desorbed and the desorption were calculated to obtain the values as shown in Table 8.



Table 8

5	<u>Adsorption</u>		<u>Desorption</u>	
	F conc.	Fluorine	Adsorbed amount	Total desor-
	(mmol/l)	removal	(mmol/g-adsorbent)	bed amount
		percentage		tion
10		(%)		(mmol)
				percen-
				tage(%)
15	1.90	81.0	3.90	22.5
				97.0

20 Method for preparation of the adsorbent:

A polyacrylonitrile was dissolved in 10 wt. % of dimethylformamide, and hydrous cerium oxide (the same substance as in Example 1) was added in an amount of 4-fold of the weight of the polymer, followed by thorough stirring, to be dispersed therein. Said mixture was formed into porous beads by use of water as the coagulation bath.

Example 20

30 A fluorine adsorbent having hydrous cerium oxide carried on a matrix of an ethylene-vinyl alcohol copolymer containing 38 mole % of ethylene at a proportion of 0.3 g/ml-adsorbent was prepared, and an example of fluorine adsorption operation by use thereof is explained below.

A column of 10 mm $\phi$  diameter was filled with 15 ml of the above adsorbent, and solutions containing hydrofluoric acid at 100 mg/liter as fluorine; adjusted to various pH's with aqueous sodium hydroxide, were passed through the column, respectively, under the conditions of 20 °C and a space velocity of 10 hr<sup>-1</sup>.  
 35 The amount of the solutions passed per 1 ml of the adsorbent until the fluorine concentration in the treated water became 1 ppm were determined to obtain the results as shown in Table 9.

Table 9

40		<u>pH of solution</u>	<u>Amount of water treated</u>
			(ml-eluate/ml-adsorbent)
45	Example 20-a	3	250
	Example 20-b	4	200
	Example 20-c	5	100
50	Example 20-d	6	40

Next, subsequent to the adsorption operation of Example 18-a, an aqueous sodium hydroxide of 240 mmol/liter was passed under the condition of a space velocity of 3 hr<sup>-1</sup> to desorb fluoride ions adsorbed. As the result, the total fluorine concentration in the desorbed solution was as high as 3500 ppm, with the desorption percentage being 100 %. The amount of the alkali necessity for desorption was found to be 1.3-fold in terms of the equivalent ratio relative to fluorine.

Method for preparation of adsorbent:

An ethylene-vinyl alcohol copolymer (ethylene: 38 mole %) was dissolved in dimethyl sulfoxide at a concentration of 11 wt. %, and hydrous cerium oxide (the same substance as in Example 1) was added in an amount of 4-fold of the weight of the polymer, followed by thorough stirring, to be dispersed therein to form a slurry. Said slurry was formed into porous beads by use of water as the coagulation bath.

## Examples 21 - 22

Examples of precipitation separation by addition of calcium ions with the use of the eluate with pH 6.7 and a fluoride concentration of 3500 ppm obtained by the column desorption method in Example 20 are shown.

Precipitation separation of fluorine was performed by adding various amounts of calcium chloride or calcium hydroxide and stirring the mixture at 20 °C for 30 minutes. The results are shown in Table 10.

Table 10

	<u>Calcium compound added</u>	<u>Amount of Ca<sup>2+</sup> added/ F<sup>-</sup> equiva- lent ratio</u>	<u>Residual fluorine conc. in filtrate (mg/liter)</u>
Example 21a	Calcium chloride	1	46
Example 21b	"	2	19
Example 21c	"	3	13
Example 21d	"	5	12
Example 21e	"	10	12
Example 22a	Calcium hydroxide	2	19
Example 22b	"	3	18

## Example 23

Examples of recovery of alkali solutions performed with the use of the eluate with pH 6.7 and a fluoride concentration of 3500 ppm obtained by the column desorption method in Example 20 are shown.

The compositions of the alkali solutions recovered by adding various amounts of calcium hydroxide and stirring the mixture at 20 °C for 30 minutes were measured. The results are shown in Table 11.

Table 11

5	Ca added	pH	Alkaline solution recovered			
			Ca <sup>2+</sup> /F <sup>-</sup>	[OH <sup>-</sup> ]	[F <sup>-</sup> ]	[Ca <sup>2+</sup> ]
			equivale-	mmol/l	mmol/l	mmol/l
			nt ratio			
10	Example 23a	2	12.1	11	1.6	2.1
	Example 23b	2	13.2	123	1.0	3.7
15	Example 23c	2	13.8	621	0.9	3.5
	Example 23d	3	13.2	121	1.0	4.2
20	Example 23e	5	13.3	133	1.0	5.3

## Example 24

25 An adsorbent having hydrous yttrium fluoride (the same substance as in Example 4) carried on a matrix of polyacrylonitrile at a proportion of 0.3 g/ml-adsorbent was prepared, and fluorine adsorption, regeneration operation, precipitation separation of fluorine in eluate and recovery of alkali solution were performed by use thereof as shown below.

30 A column of 10 mm  $\phi$  diameter was filled with 15 ml of the above adsorbent, and a starting solution containing sodium fluoride at 100 ppm as fluoride ions and adjusted to pH 3 was passed through the column under the condition of a space velocity of 30 hr<sup>-1</sup>. As the result, the amount of the treated solution until the fluoride ion concentration in the treated water at the column outlet became 1 ppm was found to be 120-fold per 1 ml of the adsorbent, and the amount of fluorine adsorbed was 12 mg/ml-adsorbent.

35 Next, the above adsorbent having fluorine adsorbed thereon was subjected to desorbing regeneration by use of the alkali solution which was recovered as described below. The alkali solution contained 130 mmol/liter of hydroxide ions, 0.1 mmol of calcium ions and 1 mmol/liter of fluoride ions. As the result of passage of said recovered alkali solution in an amount of 6.7-fold volume of the adsorbent volume under the conditions of a space velocity of 2 hr<sup>-1</sup>, the eluate obtained contained sodium fluoride as the main component at an average fluoride ion concentration of 95 mmol/liter at pH 6.8, with desorption percentage 40 of fluorine being 100 %.

For recovery of the alkali solution from said eluate, 47.5 mmol/liter (Ca<sup>2+</sup>/F<sup>-</sup> = 2 equivalent ratio) of calcium hydroxide was added and the mixture was stirred at 20 °C for 30 minutes. As the result, the fluoride ions of sodium fluoride in the eluate were precipitated as calcium fluoride, and sodium was recovered as sodium hydroxide. The alkali solution recovered had a composition of 130 mmol/liter of sodium hydroxide, 45 3.7 mmol/liter of calcium ions and 1 mmol/liter of fluoride ions.

Next, by passing the above alkali solution through the column of 10 mm  $\phi$  diameter filled with 10 ml of the same adsorbent as used in fluoride adsorption under the condition of a space velocity of 30 hr<sup>-1</sup>, an alkali solution with a calcium ion concentration of 0.1 mmol/liter was obtained in an amount of 80-fold of the volume of the adsorbent to be recovered as the alkali solution for desorbing regeneration of the adsorbent 50 after fluorine adsorption. The concentrations of sodium hydroxide and fluorine were not changed by this operation.

As described above, the adsorbent used in the process of the present invention has great capacity for adsorption of fluorine and fluorine compounds, and besides its selectivity is also high. Further, the adsorbent having fluorine adsorbed thereon can readily be subjected to desorption of fluoride ions by 55 contact with an aqueous alkali solution to be used repeatedly, and therefore it can be used suitably as the method for separating efficiently and economically fluorine from water containing a minute amount of fluorine dissolved therein.

Also, in the treating method of the present invention, fluorine compounds can be separated from the

highly concentrated fluorine containing liquor formed in the regeneration step of the adsorbent and its filtrate can be recycled as the regenerating liquor of the adsorbent, and therefore it is a closed fluorine treating process, being extremely efficient and highly economical substantially without use of a regenerating chemical for the adsorbent.

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## Claims

1. A process for separating dissolved fluorine and/or fluorine compounds which comprises: bringing a solution having a pH of 2 to 7 and containing fluorine and/or fluorine compounds dissolved therein into  
10 contact with a hydrated rare earth oxide, a hydrous rare earth fluoride and/or a hydrous rare earth phosphate as the adsorbent.
2. A process according to Claim 1, wherein the rare earth element is at least one selected from Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.
- 15 3. A process according to Claim 1, wherein the adsorbent is hydrous cerium oxide.
4. A process according to Claim 1, wherein the adsorbent is hydrous cerium fluoride.
- 20 5. A process according to Claim 1, wherein the adsorbent is yttrium hydroxide.
6. A process according to Claim 1, wherein the adsorbent is hydrous yttrium fluoride.
7. A process according to Claim 1, wherein the adsorbent is lanthanum hydroxide.
- 25 8. A process according to Claim 1, wherein the adsorbent is hydrous lanthanum fluoride.
9. A process according to Claim 1, wherein the adsorbent is a hydrous rare earth oxide obtained from a starting material of a mixture of rare earth chlorides.
- 30 10. A process according to Claim 1, wherein the adsorbent is a hydrous rare earth fluoride or a hydrous rare earth phosphate obtained from a starting material of a mixture of rare earth chlorides.
11. A process according to Claim 10, wherein the adsorbent is hydrous cerium phosphate.
- 35 12. A process according to Claim 1, wherein the adsorbent is carried on a porous material.
13. A process according to Claim 12, wherein the porous material is an organic polymeric material.
- 40 14. A process according to Claim 13, wherein the organic polymeric material is selected from polyamide, cellulose resin, polysulfone, polyacrylonitrile and ethylene-vinyl alcohol copolymer.
15. A process according to Claim 14, wherein the form of the porous material is spherical.
- 45 16. A process according to Claim 15, wherein the porous material has a porosity of 0.5 to 0.85 and a bead size of 0.1 to 5 mm.
17. A process for treating dissolved fluorine, which comprises bringing an aqueous solution of pH 2 to 7 containing fluorine and/or fluorine compounds dissolved therein into contact with an adsorbent comprising a hydrated rare earth oxide, a hydrous rare earth fluoride and/or a hydrous rare earth phosphate to  
50 separate fluorine and/or fluorine compounds by adsorption, and bringing said adsorbent having adsorbed fluorine and/or fluorine compounds thereon into contact with an alkali solution of pH 10 to 14 to desorb the adsorbed fluorine and/or fluorine compounds, thereby regenerating said adsorbent.
- 55 18. A process according to Claim 17, further comprising a step of separating fluorine and/or fluorine compounds by addition of a precipitating agent for fluorine and/or fluorine compounds to the alkali solution containing desorbed fluorine and/or fluorine compounds.

19. A process according to Claim 18, further comprising a step of recovering the alkali solution as a regenerating solution for the adsorbent having adsorbed fluorine and/or fluorine compounds thereon.

20. A process according to Claim 17, wherein the alkali solution contains at least one alkali selected from sodium hydroxide, potassium hydroxide, ammonium hydroxide and organic amines.

21. A process according to Claim 18, wherein the precipitating agent for fluorine and/or fluorine compounds is at least one compound selected from salts, oxides and hydroxides of calcium, magnesium and aluminium.

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## Revendications

1. Procédé de séparation du fluor et/ou de composés fluorés dissous, qui consiste à mettre une solution ayant un pH de 2 à 7 et contenant du fluor et/ou des composés fluorés dissous en son sein en contact avec un oxyde de terre rare hydraté, avec un fluorure de terre rare hydraté et/ou avec un phosphate de terre rare hydraté servant d'adsorbant.

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2. Procédé suivant la revendication 1, dans lequel l'élément de terre rare est au moins un élément choisi parmi Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, et Lu.

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3. Procédé suivant la revendication 1, dans lequel l'adsorbant est de l'oxyde de cérium hydraté.

4. Procédé suivant la revendication 1, dans lequel l'adsorbant est du fluorure de cérium hydraté.

5. Procédé suivant la revendication 1, dans lequel l'adsorbant est de l'hydroxyde d'yttrium.

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6. Procédé suivant la revendication 1, dans lequel l'adsorbant est du fluorure d'yttrium hydraté.

7. Procédé suivant la revendication 1, dans lequel l'adsorbant est de l'hydroxyde de lanthane.

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8. Procédé suivant la revendication 1, dans lequel l'adsorbant est du fluorure de lanthane hydraté.

9. Procédé suivant la revendication 1, dans lequel l'adsorbant est un oxyde de terre rare hydraté obtenu à partir d'une matière première constituée d'un mélange de chlorures de terre rare.

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10. Procédé suivant la revendication 1, dans lequel l'adsorbant est un fluorure de terre rare hydraté ou un phosphate de terre rare hydraté obtenu à partir d'une matière première constituée d'un mélange de chlorures de terre rare.

11. Procédé suivant la revendication 10, dans lequel l'adsorbant est du phosphate de cérium hydraté.

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12. Procédé suivant la revendication 1, dans lequel l'adsorbant est sur un support en matériau poreux.

13. Procédé suivant la revendication 12, dans lequel le matériau poreux est un polymère organique.

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14. Procédé suivant la revendication 13, dans lequel le polymère organique est un polyamide, une résine de cellulose, une polysulfone, un polyacrylonitrile ou un copolymère d'éthylène et d'alcool vinylique.

15. Procédé suivant la revendication 14, dans lequel le matériau poreux est sphérique.

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16. Procédé suivant la revendication 15, dans lequel le matériau poreux a une porosité de 0,5 à 0,85 et une dimension de perle de 0,1 à 5 mm.

17. Procédé de traitement du fluor dissous, qui consiste à mettre une solution aqueuse, ayant un pH de 2 à 7 et contenant du fluor et/ou des composés fluorés dissous en son sein, en contact avec un adsorbant comprenant un oxyde de terre rare hydraté, un fluorure de terre rare hydraté et/ou un phosphate de terre rare hydraté, pour séparer du fluor et/ou des composés fluorés par adsorption, et à mettre l'adsorbant sur lequel est adsorbé du fluor et/ou des composés fluorés en contact avec une

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solution alcaline ayant un pH de 10 à 14, pour désorber le fluor et/ou les composés fluorés adsorbés de manière à régénérer l'adsorbant.

18. Procédé suivant la revendication 17, comprenant en outre un stade de séparation du fluor et/ou des composés fluorés, par l'addition d'un agent de précipitation du fluor et/ou des composés fluorés à la solution alcaline contenant le fluor et/ou les composés fluorés désorbés.

19. Procédé suivant la revendication 18, comprenant en outre un stade de récupération de la solution alcaline servant de solution de régénération de l'adsorbant, sur lequel est adsorbé du fluor et/ou des composés fluorés.

20. Procédé suivant la revendication 17, dans lequel la solution alcaline contient au moins une substance alcaline choisie parmi l'hydroxyde de sodium, l'hydroxyde de potassium, l'hydroxyde d'ammonium et les amines organiques.

21. Procédé suivant la revendication 18, dans lequel l'agent de précipitation du fluor et/ou des composés fluorés est au moins un composé choisi parmi les sels, les oxydes et les hydroxydes de calcium, de magnésium et d'aluminium.

## 20 Patentansprüche

1. Verfahren zur Abtrennung von gelöstem Fluor und /oder gelösten Fluorverbindungen, bei dem man eine Lösung mit einem pH von 2 bis 7 und einem Gehalt an Fluor und/oder Fluorverbindungen, die darin gelöst sind, mit einem hydratisierten Seltenerdenoxid, einem wasserhaltigen Seltenerdenfluorid und/oder einem wasserhaltigen Seltenerdenphosphat als Adsorbens in Berührung bringt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß es sich bei dem Seltenerdenelement um mindestens 1 Element von Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb und Lu handelt.

3. Verfahren nach Anspruch 1, bei dem das Adsorbens wasserhaltiges Ceroxid ist.

4. Verfahren nach Anspruch 1, bei dem das Adsorbens wasserhaltiges Cerfluorid ist.

5. Verfahren nach Anspruch 1, bei dem das Adsorbens Yttriumhydroxid ist.

6. Verfahren nach Anspruch 1, bei dem das Adsorbens wasserhaltiges Yttriumfluorid ist.

7. Verfahren nach Anspruch 1, bei dem das Adsorbens Lanthanhydroxid ist.

8. Verfahren nach Anspruch 1, bei dem das Adsorbens wasserhaltiges Lanthanfluorid ist.

9. Verfahren nach Anspruch 1, bei dem das Adsorbens ein wasserhaltiges Seltenerdenoxid ist, das aus einem Ausgangsmaterial eines Gemischs von Seltenerdenchloriden erhalten worden ist.

10. Verfahren nach Anspruch 1, bei dem das Adsorbens ein wasserhaltiges Seltenerdenfluorid oder ein wasserhaltiges Seltenerdenphosphat ist, das aus einem Ausgangsmaterial eines Gemischs von Seltenerdenfluoriden erhalten worden ist.

11. Verfahren nach Anspruch 10, bei dem das Adsorbens wasserhaltiges Cerphosphat ist.

12. Verfahren nach Anspruch 1, bei dem das Adsorbens ein poröses Material auf einem Träger ist.

13. Verfahren nach Anspruch 12, bei dem das poröse Material ein organisches Polymermaterial ist.

14. Verfahren nach Anspruch 13, bei dem das organische Polymermaterial unter Polyamid, Celluloseharz, Polysulfon, Polyacrylnitril und Ethylen/Vinylalkohol-Mischpolymer ausgewählt ist.

15. Verfahren nach Anspruch 14, bei dem die Form des porösen Materials kugelförmig ist.
16. Verfahren nach Anspruch 15, bei dem das poröse Material eine Porosität von 0,5 bis 0,85 und eine Perlengröße von 0,1 bis 5 mm besitzt.
- 5 17. Verfahren zur Behandlung von gelöstem Fluor, bei dem man eine wässrige Lösung mit einem pH von 2 bis 7 mit einem Gehalt an Fluor und/oder Fluorverbindungen, die darin gelöst sind, mit einem Adsorbens aus der aus hydratisiertem Seltenerdenoxid, wasserhaltigem Seltenerdenfluorid und/oder wasserhaltigem Seltenerdenphosphat bestehenden Gruppe zur Abtrennung von Fluor und/oder Fluor-  
10 verbindungen durch Adsorption in Berührung bringt, das Adsorbens mit adsorbiertem Fluor und/oder adsorbierten Fluorverbindungen auf dem Adsorbens mit einer Alkalilösung mit einem pH von 10 bis 14 in Berührung bringt, das adsorbierte Fluor und/oder die adsorbierten Fluorverbindungen desorbiert und dadurch das Adsorbens regeneriert.
- 15 18. Verfahren nach Anspruch 17, dadurch gekennzeichnet, daß als weitere Stufe vorgesehen ist, daß man das Fluor und/oder die Fluorverbindungen durch Zugabe eines Fällungsmittels für Fluor und/oder Fluorverbindungen zur Alkalilösung mit einem Gehalt an desorbiertem Fluor und/oder Fluorverbindungen abtrennt.
- 20 19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß eine weitere Stufe vorgesehen ist, bei der man die Alkalilösung als Regenerierlösung für das Adsorbens rückgewinnt, das adsorbiertes Fluor und/oder adsorbierte Fluorverbindungen trägt.
- 25 20. Verfahren nach Anspruch 17, bei dem die Alkalilösung mindestens ein Alkali aus der durch Natriumhydroxid, Kaliumhydroxid, Ammoniumhydroxid und organischer Amine gebildeten Gruppe enthält.
21. Verfahren nach Anspruch 18, bei dem das Fällungsmittel für Fluor und/oder Fluorverbindungen mindestens eine Verbindung aus der durch Salze, Oxide und Hydroxide von Kalzium, Magnesium und Aluminium gebildeten Gruppe ist.

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FIG. 1

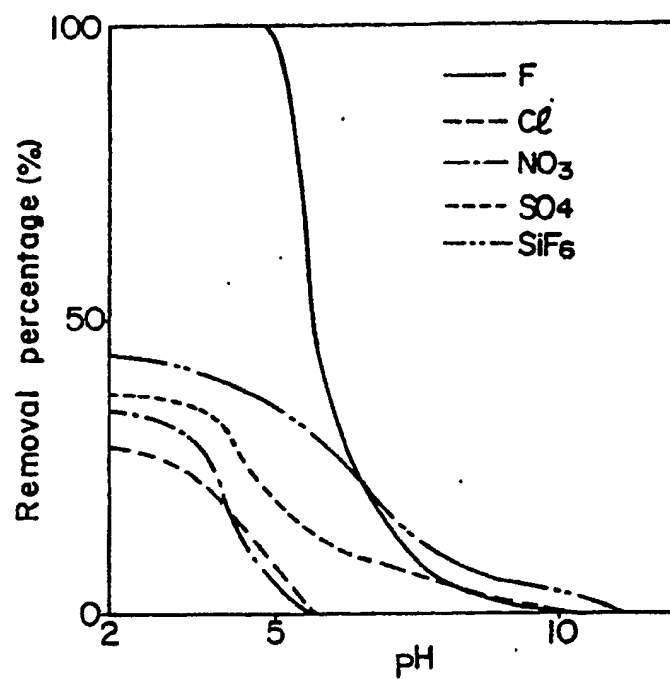


FIG. 2

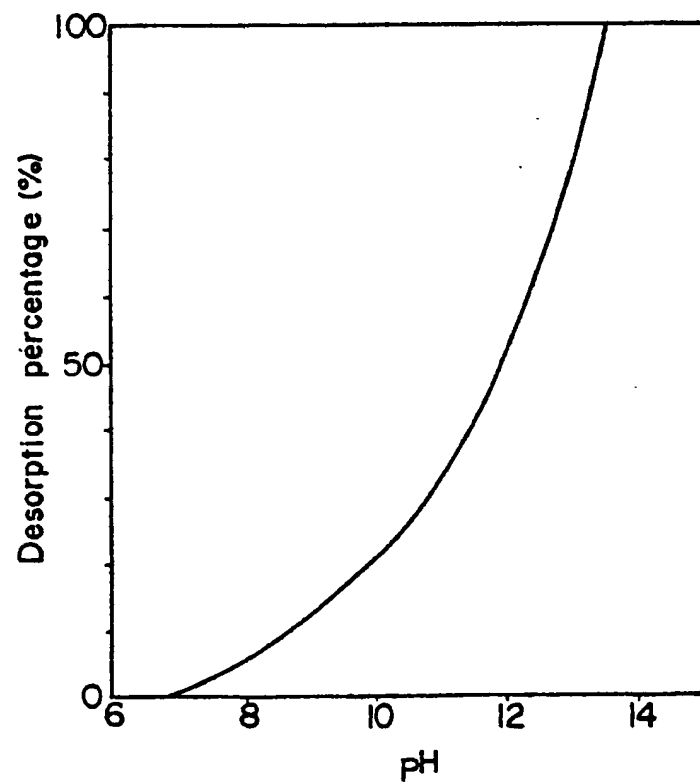




FIG. 3a

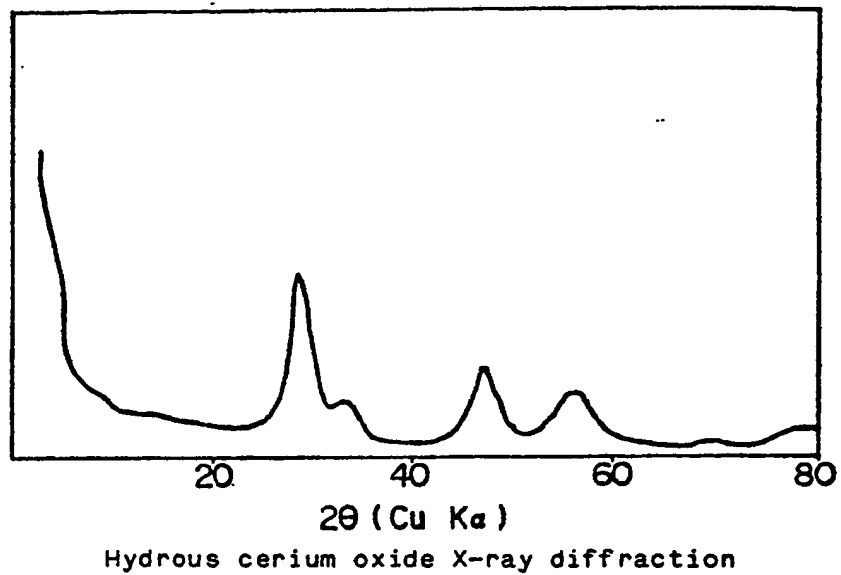
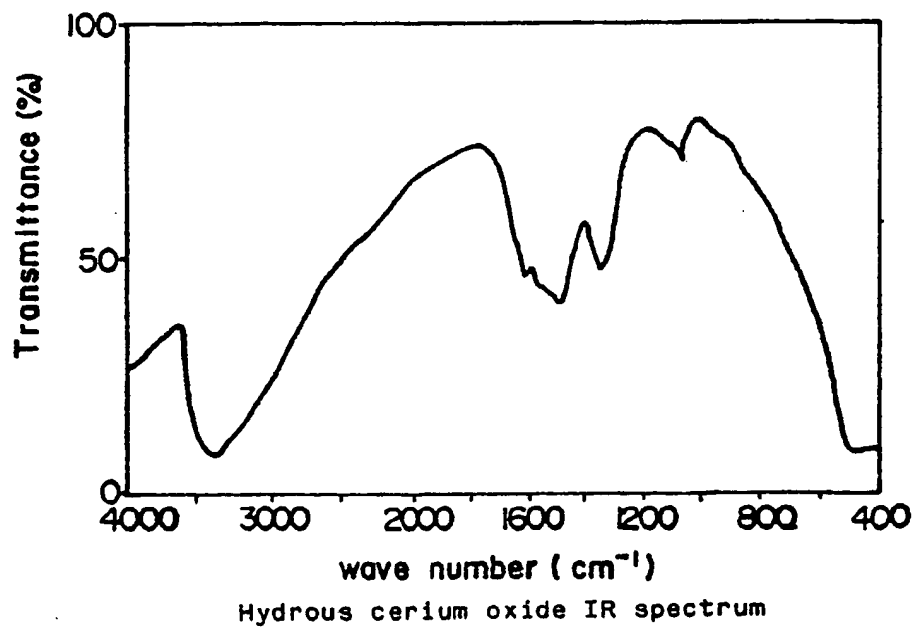
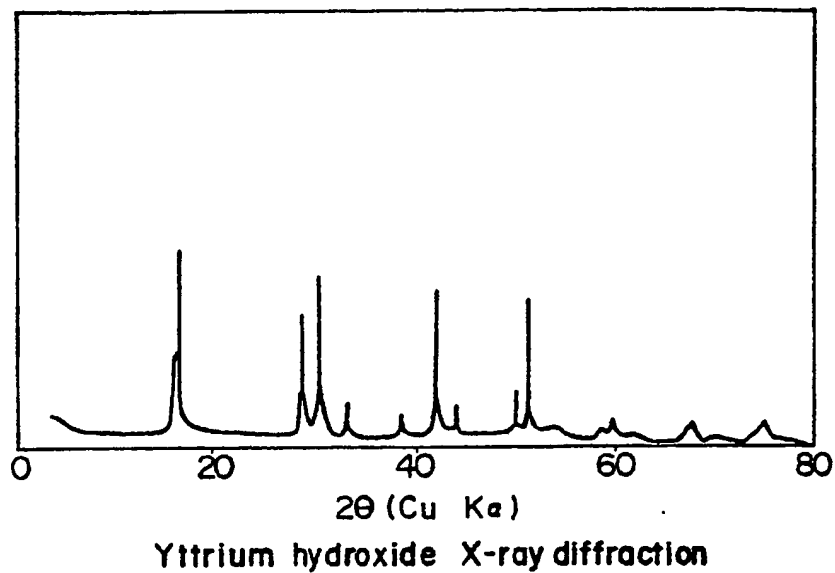


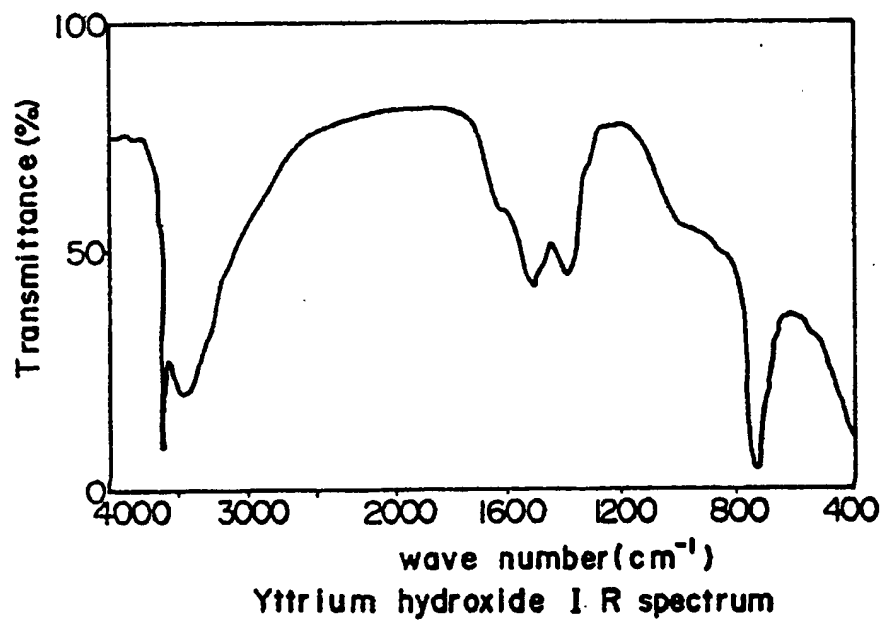
FIG. 3b



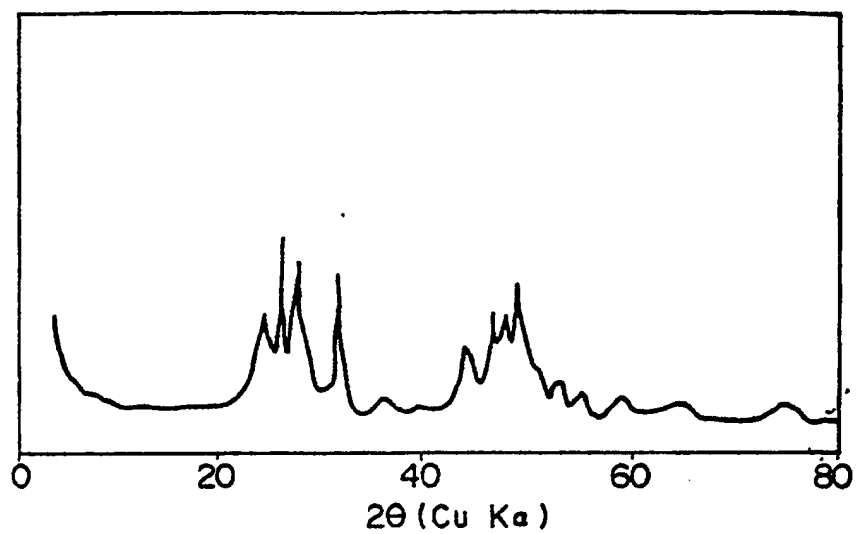
**FIG. 4a**



**FIG. 4b**

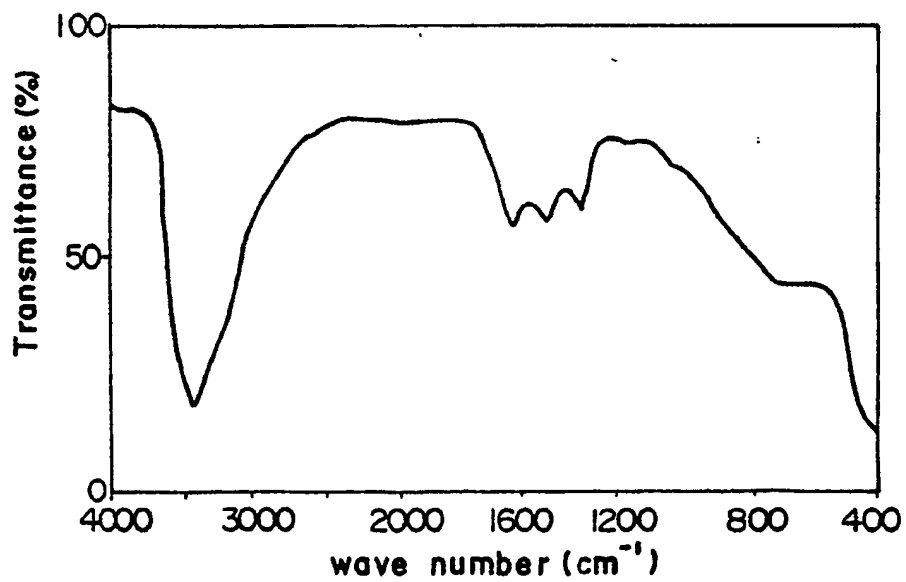


**FIG. 5a**



**Hydrous yttrium fluoride X-ray diffraction**

**FIG. 5b**



**Hydrous yttrium fluoride I R spectrum**

FIG. 6

